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Adsorption of Ammonium Nitrogen from Aqueous Systems Using Chitosan-Bentonite Film Composite

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Abstract

In this work, a novel composite adsorbent based on chitosan and bentonite nanoclay was prepared in the form of thin films and its efficacy for removing ammonium-nitrogen ($NH4^{+}$-N) from aqueous solution was investigated using batch adsorption experiments. The characterization of both chitosan and chitosan nanocomposite have been done with Thermogravimetric analyser and FTIR spectra. In the adsorption test, the effect of pH, initial concentration, and adsorbent concentration on NH_4^{+}-N removal was studied. A comparison between as-prepared adsorbent and adsorbent modified with nanoclay was also carried out. The optimum condition for maximum adsorption of ammonia nitrogen from aqueous solution was found to be 15ppm, 0.5g, & 6 for initial concentration, adsorbent concentration and pH respectively. All information obtained gives an indication that the composite can be used as a novel type, fast-responsive and high-capacity sorbent material for NH4 $^{+}$-N removal. As ammonium nitrogen is a good nutrient for plants and chitosan is a biopolymer the exhaust adsorbents can be reused as a fertilizer in agricultural purpose.

Keywords: Chitosan; Adsorption; Ammonium Nitrogen; Bentonite

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1. Introduction

The disposal of of nitrogen compounds (Nitrate,Nitrite and Ammonia nitrogen) directly from water plants or indirectly from agriculture and leaching from sludge deposited in landfill and fields have resulted in eutrophication of water bodies[1]. It has been widely reported that ammonium nitrogen (NH_4 +-N) is a very common chemical form in aquatic ecosystems and its toxic effect on life is very high[2]. Total removal or at least a significant reduction of NH_4+-N is thus very important prior to disposal into streams, lakes, seas and land surface. Up to now, the main treatment methods to remove/reduce NH_4^+-N involve reverse osmosis, biological nitrification, denitrification, air stripping, chemical treatment, ion-exchange and supercritical water oxidation[3]. The easy operation technology, low energy input & cost, high safety makes the adsorption process a superior solution for ammonium stripping from aqueous systems. The key factor in adsorption technology, is adsorbent. In this work adsorbent material is a biopolymer and adsorbate is a nutrient, so that the exhausted adsorbent can be utilized as a fertilizer agent[5].

From the ancient to the modern time, clay minerals have been used in building materials, earthenware, ceramic products, cement, adsorbent, cosmetics, rubber, paper, paints, etc. The application of particular clay minerals depends on their physical and chemical properties and these properties strongly depend on the structure and composition. The main clay mineral constituents in bentonite are sodium montmorillonite (Na-MMt) and calcium montmorillonite (Ca-MMt)[7]. Bentonite has been used for the removal of various hazardous substances from water or wastewater[4]. High adsorption capacity of bentonite is due to the high charge on their lattice structure and high cation exchange capacity (CEC).In general, normal cation exchange capacity of bentonite is between 40and 130 meq/100.

This work is mainly aimed on the preparation of a biopolymer nanoclay composite and its application for NH4+-N removal from aqueous solution. The characterization of the adsorbents are done with TGA and FTIR spectroscopy. The effects of system parameters, such as pH, values of initial NH4+-N solutions and composition of both adsorbents were also systematically investigated

2.Materials and methods

2.1 Materials

Ammonium Chloride, Sodium hydroxide, Red mercuric Iodide, Potassium Iodide and Bentonite nanoclay was purchased from Sigma Aldrich.. Ammonium chloride was dehydrated at 70^0C prior to use. Commercial grade Chitosan (with a degree of deacetylation of 0.87 and average molecular weight of 3×10^5 was brought from India Sea Food,Kochi. Both chitosan and nanoclay were used as received

2.2 Preparation of Stock ammonia solution

The stock solution of NH_4^+-N (1000 mg/L) was prepared by dissolving 3.8190 g dried ammonium chloride (NH_4Cl) in 1 liter of deionized water. The solution was stored in a round bottom flask. The experimental solutions were prepared by diluting the stock solution with deionized water when necessary as per the requirement.

2.3. Preparation of chitosan film

Chitosan film was prepared by adding Chitosan into a 1% acetic acid solution. Acetic Acid Solution(1%) was prepared by adding 1ml of glacial acetic acid into 99ml distilled water. Later 2gm of Chitosan was added in 98ml of 1% Acetic acid solution and was kept in a sonicator for 30minutes allowing the chitosan to completely dissolve into the solution[4,8]. The resulting solution was poured into a glass plate and was dried at 70^0C for 4 hours in an oven to get the film. The film was then peeled from the glass plate and was washed and dried to use for the adsorption experiments. Film was then cut into small pieces with equal surface area of 1 sq.cm.

Fig.1.Chitosan-bentonite Films

2.5Adsorption experiment

The adsorption experiments were performed using the batch equilibration method[9]. In this method, adsorbent was mixed with 50ml of ammonium chloride stock solution. The mixtures were sealed and shaken at 200 rpm and at room temperature for desired time period to reach equilibrium. The effect of pH on ammonia concentration was studied by keeping the other factors at a constant value and samples for different pH was analysed.[13] Similar experiments were conducted for the study of initial concentration, and adsorbent concentration keeping the shaking speed at 200 rpm and at room temperature.

2.6. Analysis using UV Spectrophotometer

Calibration of stock ammonia solution was done using UV Spectrophotometer. Ammonia was calibrated at 5pm, 10ppm, 15ppm, 20ppm & 25ppm at 450nm wavelength. Since the UV Spectrophotometer cannot be used to identify the concentration of adsorbent present in it for colourless solutions we add Nesslers Reagent in order to find out the adsorbent concentration present in the stock solution (2ml/50ml of stock solution)[10].Once the Reagent is added to the ammonia solution its colour changes to pale yellow. The colour of the solution depends on the amount of ammonia present in the solution which helps the UV Spectrophotometer to identify the amount of ammonia left over after adsorption. The graph shown below is the calibration curve of ammonia which is later used to determine the concentration of ammonia in the stock solution after the process of adsorption.

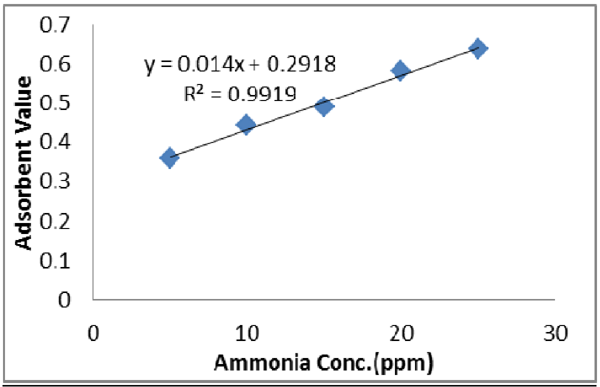

Fig.2. Ammonia Calibration Curve

Sample analysis is done once the calibration process is complete. Samples were kept inside the UV Spectrophotometer for analysis and the final concentration of ammonia can be obtained resulting in the ammonium adsorption capacity using chitosan films and nanoclay modified chitosan films.

3. Results and discussion

3.1.Characterization of Adsorbents

TGA was done for both the adsorbents used for removal of ammoniacal nitrogen from aqueous solution. TGA is used to check the thermal stability of any materials, adsorbents here. From the graph below we can see that with the rise in temperature the weight percentage of the adsorbent decreasing and comes down to zero at a temperature of 670 °C. But in the case of chitosan modified using nnoclay shows a better thermal stability because the weight percent have not come down to zero even at 800 °C. The mass of each sample was 6-8 mg. The carrier gas was nitrogen with a flow rate of 50mL/min. The samples were heated from 30 °C to 800 °C with a rate of 10 °C per minute.

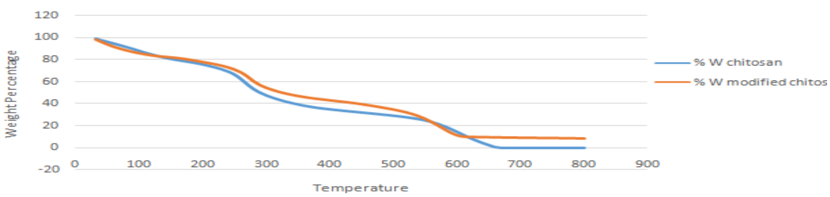

Fig.3.TGA for Both adsorbents

FTIR is a technique which is used to obtain an infrared spectrum of adsorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas[16]. The FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. Most changes occurring on the adsorbent are reflected in the broad band present between 1000 and 1500 cm-1 for chitosan and modified chitosan film respectively. From the spectrum it can be found that the distinctive adsorption bands appear at 1642 cm^{-1}(amide I),1541cm^{-1}(-NH2 bending), and 1407 cm^{-1} (amide III). The adsorption band at 1017 cm-1 is a characteristic of its saccharine structure

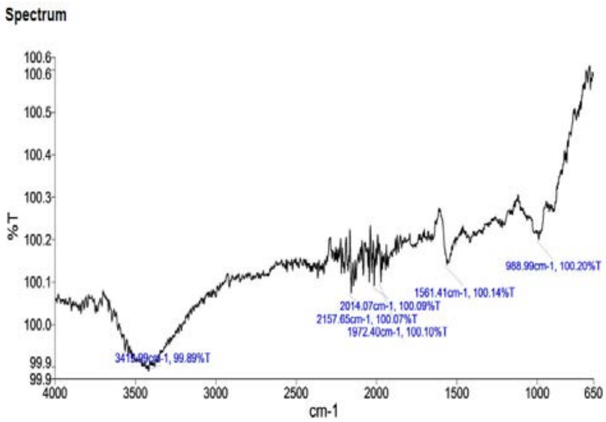

Fig.4.FTIR Analysis

3.2.Influence of pH

Effect of different pH values on the adsorption capacity of NH_4+-N onto Chitosan film and modified chitosan film (T=30◦C,t=4 hours , C_0 = 15 mg/L, adsorbent dose = 0.5mg/50 ml, 200 rpm) has sown in Fig 5. It can be seen that the amount of NH_4^+-N removed by both the adsorbents at different pH values is exhibiting a same trend. Maximum adsorption is obtained at a pH of 6 on both the adsorbents and after that the adsorption is found to show a decreasing trend in both cases. A rise in the removal rate was observed at higher pH of 9,this may be because at higher pH values, ammonium ions (NH_4+) tend to be transformed to ammonia gas[5,6]. The pH value of original NH_4+-N solution lies between 5.0 and 7.0. Therefore, the pH value of working NH_4 +-N solution is not necessary to be adjusted to a pH of 6. A maximum of 64.6 percentage was obtained when chitosan films were used as adsorbents whereas it is increased to a percentage of 98.05 for modified chitosan film using nanoclay Maximum adsorption using both adsorbents happened at a pH of 6. Later this pH value was kept at constant and the effect of other parameters was studied.

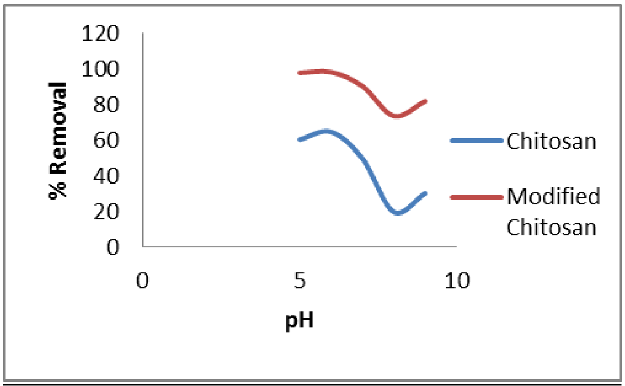

Fig.5.Influence of pH for ammonia adsorption

3.3 .Influence of Initial Concentration

The effect of initial concentration on ammonium nitrogen adsorption is measured by varying the concentration of ammonium nitrogen solution from 5ppm to 25ppm, keeping pH at a constant value of 6. The experiments were carried out at 30 °C with an adsorbent dose of 0.1 g/50mL, an agitation speed at 200 rpm for a contact time of 4 hours. For each initial aqueous ammonium concentration, (C_0 between 5 and 25mg/L), the process of ammonium adsorption was found to increase till 15 mg/L and shows a constant removal upto 25 mg/L showing that it has reached a state of equilibrium.. After the concentration of 15 mg/L, the ammonium adsorption continues, but with a much slower rate[14]. The adsorption rate is 69.87% for chitosan film and 83.87% for modified chitosan. Raising the initial ammonium concentration from 5 to 25 mg/l allows the adsorbents to increase their adsorption capacities from 11.8 to 65% and 78.4% to 83.13% for both chitosan films and modified chitosan-nanoclay films respectively[12].. In fact, it has a high adsorption capacity (83.13 %) for an initial concentration of 15 mg/L, and at pH 6. Compared to other adsorbents, such as mineral and organic materials, this adsorption capacity is relatively high and ammonium is more efficiently removed from aqueous solutions.

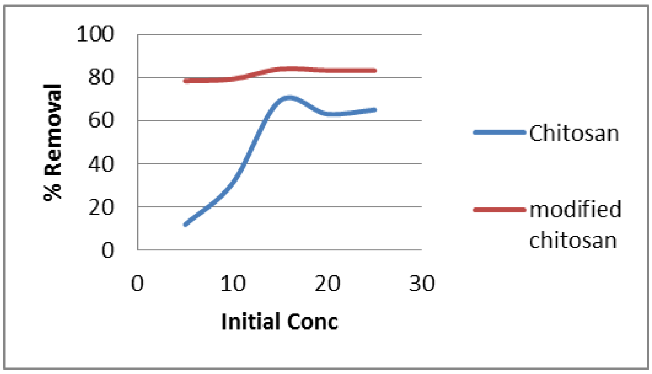

Fig.6.Influence of Initial Conc. for ammonia adsorption

3.4. Influence of Adsorbent Concentration

Effect of change in adsorbent concentration on percentage removal of ammonia from aqueous solution using chitosan and modified chitosan was studied by keeping other parameters in its optimum range. The percentage removal is found to be increasing with increase in adsorbent concentration. The adsorption test is conducted with a varying adsorbent concentration from 0.1g to 0.5g keeping the Initial concentration at 15mg/L, temperature at 30^{o}C, shaking speed at 200rpm for 4 hours and at a pH of 6. The graph shown in fig 7 shows a steady adsorption for ammonia nitrogen using both chitosan films and modified chitosan films. For 0.5g of chitosan and modified chitosan films maximum ammonia nitrogen removal is obtained as 43.19% and 82.11%.The percentage removal with modified chitosan film is almost double which shows that more surface area is available for adsorption process[13].

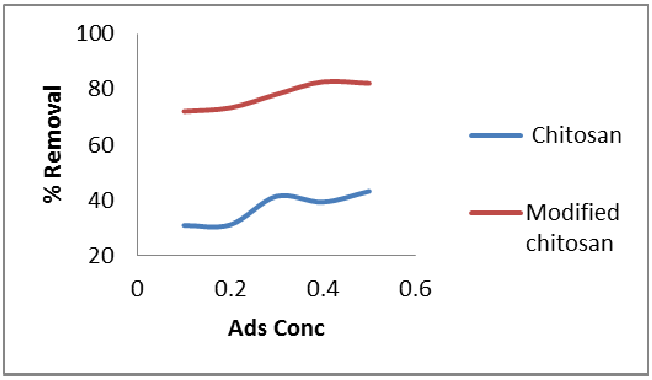

Fig 7. Influence of adsorbent Conc. for ammonia adsorption

4.Conclusions

A novel bentonite nanoclay composite adsorbent was prepared with the aim of minimizing the negative impact of nitrogen pollution and improving fertilizer use efficiency. The thermal stability of adsorbent was found out using a thermogravimetric analyzer (TGA). The morphological analysis was done with Fourier transform infrared spectrometer (FTIR). The capacity of chitosan and chitosan-bentonite film composite to take up ammonia nitrogen from aqueous solution has been investigated in this work. The results shows that removal of ammonium nitrogen from aqueous solutions varies with changes in initial concentration, adsorbent concentration and pH .The optimum obtained was 6. The stripping of ammonia nitrogen for a solution of concentration 15 mg/l with 0.5g of chitosan and chitosan films is reported as 43.19% and 82.11%.The percentage removal with modified chitosan film is almost double which shows that more surface area is available for adsorption process.. Ammonium removal using these types of adsorbents can be applied for commercial purpose as well. The exhausted adsorbent enriched with nitrogen can be recovered and reused as a fertilizer[15].

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